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Benzotriazolate cage complexes of tin(II) and lithium: halide-influenced serendipitous assembly†

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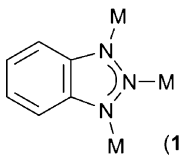
The one-pot reactions of the tin(II) halides SnX_2 (X = F, Cl, Br, I) with lithium hexamethyldisilazide, [Li(hmds)], and benzotriazole, (bta)H, produce contrasting outcomes. Tin(II) fluoride does not react with [Li(hmds)] and (bta)H, the outcome being the formation of insoluble $[Li(bta)]_\infty$. Tin(II) chloride and tin(II) bromide react with [Li(hmds)] and (bta)H in toluene to produce the hexadecametallic tin(II)-lithium cages $[(hmds)_8Sn_8(bta)_{12}Li_8X_4]\cdot(n$ toluene) [X = Cl, **3**·(8 toluene); X = Br, **4**·(3 toluene)]. The reaction of tin(II) iodide with [Li(hmds)] and (bta)H in thf solvent produces the ion-separated species $[\{(thf)_2Li(bta)\}_3\{Li(thf)\}]_2[SnI_4]\cdot(thf)$, $[\mathbf{5}]_2[SnI_4]\cdot(thf)$, the structure of which contains a cyclic trimeric unit of lithium benzotriazolate and a rare example of the tetraiodostannate(II) dianion.

Introduction

The protection of metals and alloys from corrosion is an important industrial application of the organic heterocycle benzotriazole, (bta)H.[1,2] Applications of the benzotriazolate ligand, $[bta]^-$, in the synthesis of polymetallic transition metal cage complexes are also widespread.[3,4] A common coordination mode of $[bta]^-$ involves the ligand bridging between three metals, illustrated schematically as $[(bta)M_3]$ (**1**). The natural orientation of the lone pairs on the vicinal nitrogen donors in $[bta]^-$ provides an important structure-directing influence, which allows access to a range of structurally diverse polymetallic transition metal cage complexes.



(1)

In contrast, the use of $[bta]^-$ in the coordination chemistry of the main group metals is uncommon, with only a handful of benzotriazole complexes of the s-block[5–7] and p-block[8,9] metals being known. Systematic studies of the coordination chemistry of $[bta]^-$ in p-block chemistry are unknown. A possible explanation for the paucity of studies on main group benzotriazole complexes is their poor solubility in all but the most polar solvents, such as dimethylsulphoxide (dmso)[5] and hexamethylphosphoramide (hmpa).[6] The amido character of the metal-nitrogen bonds in main group $[bta]^-$ complexes precludes the use of other polar solvents commonly used in transition metal benzotriazolate chemistry, such as alcohols and acetone.

We recently found that the bimetallic benzotriazole complex of lithium and iron(II) $[(hmds)_2Fe(bta)Li]_2$ (**2**) has good solubility in toluene even at −30 °C, owing to the presence of lipophilic hexamethyldisilazide (hmds) ligands in the structure.[7] Complex **2** was synthesized using a 'one-pot' route in which [Li(hmds)] and (bta)H were combined as solids with $[FeBr_2(thf)_2]$, and toluene solvent was subsequently added, which resulted in the formation of **2** *via* serendipitous assembly.

We now report that the general principles of the one-pot method developed for **2** can be extended to the synthesis of bimetallic $[bta]^-$ complexes of tin(II) and lithium by using SnX_2 with X = Cl or Br in reactions with [Li(hmds)] and (bta)H. These reactions produced the isostructural hexadecametallic cages $[(hmds)_8Sn_8(bta)_{12}Li_8X_4]\cdot(n$ toluene) [X = Cl, **3**·(8 toluene); X = Br, **4**·(3 toluene)]. However, when the tin(II) source was SnF_2, no reaction with [Li(hmds)] and (bta)H was observed, but with SnI_2 the outcome was the ion-separated species $[\{(thf)_2Li(bta)\}_3\{Li(thf)\}]_2[SnI_4]\cdot(thf)$, $[\mathbf{5}]_2[SnI_4]\cdot(thf)$, the structure of which contains a cyclic ladder of lithium benzotriazolate and a rare example of the saw-horse-shaped tetraiodostannate(II) dianion.

Results and discussion

The reactions between [Li(hmds)], (bta)H and the series of tin(II) halides were carried out using the same 2 : 1 : 1 stoichiometry in each case, either in toluene or thf (Scheme 1).

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† Electronic supplementary information (ESI) available: NMR spectra of compounds, full summary of crystal data and structure refinements, and crystallographic details, thermal ellipsoid plots of **3**, **4** and $[\mathbf{5}]_2[SnI_4]$. CCDC reference numbers 816705 **3**·(8 toluene); 816706 **4**·(3 toluene); 816707 $[\mathbf{5}]_2[SnI_4]\cdot(thf)$. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10400d

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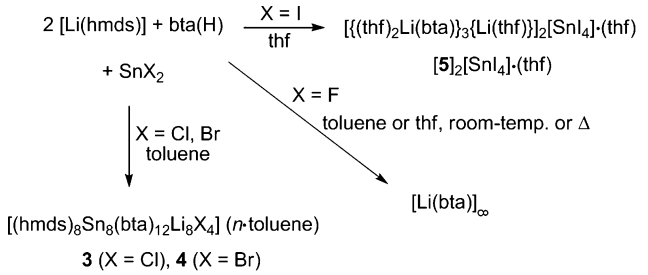

Scheme 1

The outcome of combining [Li(hmds)] and (bta)H with SnF_2 was the same irrespective of the solvent being either thf or toluene, and whether the reagents were heated under reflux or not. In these reactions, the formation of a colourless precipitate of $[Li(bta)]_\infty$ and a grey powder identical in appearance to SnF_2 were observed.

In contrast, combining [Li(hmds)] and (bta)H with $SnCl_2$ or $SnBr_2$ as solids at −78 °C and adding toluene, followed by warming the reaction mixtures to room temperature and stirring overnight, resulted in the formation of orange solutions and a fine precipitate. Removal of the precipitate by filtration, concentrating the solution and storage at −30 °C yielded yellow crystals in each case. X-ray crystallography revealed the molecular structures of the products arising from both reactions to be the hetero-bimetallic tin(II)-lithium cages $[(hmds)_8Sn_8(bta)_{12}Li_8X_4]\cdot(n$ toluene) (X = Cl, n = 8, **3**; X = Br, n = 3, **4**). Owing to the similarity of the structures of **3** and **4** only that of **3** will be described in detail.

The molecular structure of **3** (Fig. 1) consists of 250 unique non-hydrogen atoms. The eight tin(II) atoms in **3** each reside in a pyramidal environment, and they are coordinated by a terminal [hmds]$^-$ ligand, with Sn–N($SiMe_3$)$_2$ distances in the range 2.088(4)–2.110(4) Å (average 2.096 Å). Two of the tin(II) atoms in **3**, Sn(1) and Sn(3), are also complexed by a μ-chloro ligand to produce Sn(1)–Cl(1) and Sn(3)–Cl(4) bond distances of 2.5606(15) and 2.5307(15) Å, respectively, and by a nitrogen donor of a [bta]$^-$ ligand to give Sn(1)–N(37) and Sn(3)–N(8) as 2.288(5) and 2.263(5) Å, respectively. The other six tin(II) atoms are additionally coordinated by two [bta]$^-$ nitrogens to give Sn–N bond distances in the range 2.231(4)–2.323(4) Å (average 2.272 Å). Each of the twelve [bta]$^-$ ligands coordinates to lithium and tin(II) in the [(bta)M_3] mode represented by **1**; two of the twelve benzotriazolates coordinate to form [(bta)Sn_2Li] units, and ten coordinate as [(bta)$SnLi_2$].

Each of the eight lithiums in **3** resides in a distorted tetrahedral geometry. The coordination environments of Li(1) and Li(4) consist of two chloro ligands and two [bta]$^-$ nitrogens, whereas the other six lithiums are complexed by one chloro ligand and three [bta]$^-$ nitrogens. The range of Li–Cl distances is 2.307(9)–2.425(10) Å (average 2.380 Å) and the Li–N distances are in the range 1.998(10)–2.065(10) Å (average 2.033 Å). The lithium cations and the chloride ligands in **3** can be regarded as being encapsulated within an amido-tin(II) periphery, such that an $[Li_8Cl_4]$ channel runs through the cage complex from Sn(1) to Sn(3). The overall molecular structure of **3** is highly asymmetric, and although connecting the lithium cations describe a distorted bicapped octahedron, connecting the tin(II) atoms does not produce a regular polyhedral arrangement of atoms.

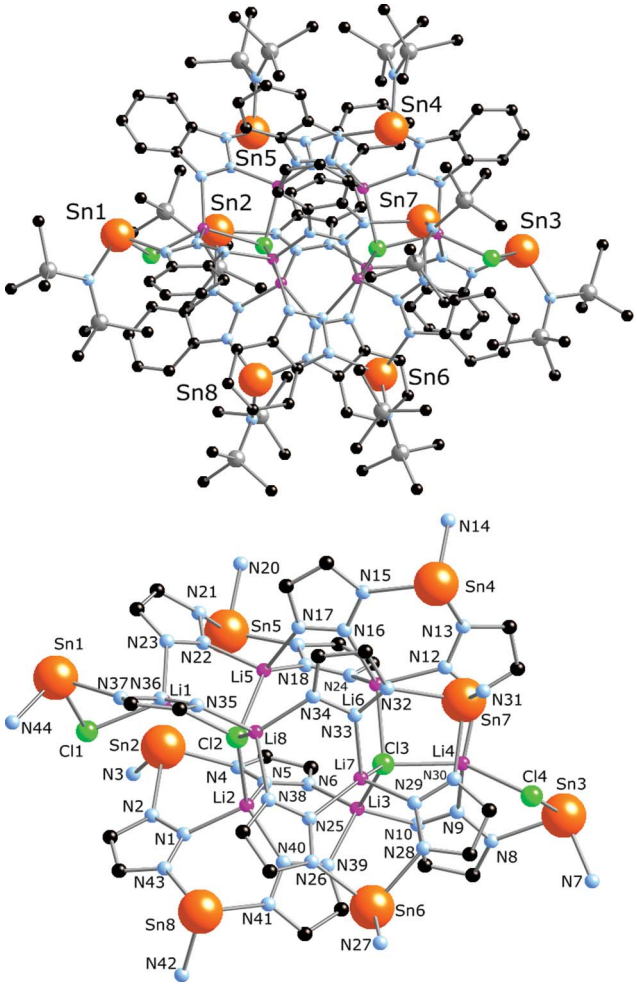

Fig. 1 Structure of **3** (upper), and expanded view of the core of **3** (lower) with $SiMe_3$ substituents and benzotriazole C_6 rings omitted. Tin = orange, lithium = pink, chlorine = green, nitrogen = blue, silicon = grey. Hydrogen atoms are omitted in both structures.

Table 1 Selected bond lengths for **3**·(8 toluene) and **4**·(3 toluene)

	3·(8 toluene)/Å[a]	**4**·(3 toluene)/Å[b]
Sn(1)–X(1)	2.5606(15)	2.6994(10)
Sn(3)–X(4)	2.5307(15)	2.7121(10)
Sn–NR_2[c]	2.088(4)–2.110(4), 2.096[d]	2.089(8)–2.129(7), 2.105
Sn–N(bta)	2.231(4)–2.323(4), 2.272	2.231(6)–2.336(6), 2.271
Li–X	2.307(9)–2.425(10), 2.380	2.452(13)–2.612(16), 2.537
Li–N	1.998(10)–2.065(10), 2.033	1.967(14)–2.072(13), 2.034

[a] X = Cl, [b] X = Br, [c] R = $SiMe_3$, [d] average.

The structure of **4** (ESI Figure S3 and Table S2†) is very similar to that of **3**, consisting of a hexadecametallic Sn_8Li_8 core, with the metal atoms bridged either by [bta]$^-$ or bromide ligands. Pertinent bond lengths are shown in Table 1.

Placing samples of **3**·(8 toluene) and **4**·(3 toluene) *in vacuo* (10^{-3} mmHg) produces polycrystalline materials, the compositions of which were shown by elemental analysis to correspond to **3** and **4**, *i.e.* complete removal of the lattice toluene molecules. Complexes **3** and **4** are insoluble in hydrocarbon and aromatic solvents, but are sufficiently soluble in thf-d_8 to enable analysis by ^{1}H, ^{13}C and ^{7}Li

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NMR spectroscopy. The low solubility of **3** and **4** combined with the low receptivity of the ^{119}Sn nucleus prevented the acquisition of meaningful ^{119}Sn NMR spectra. The ^{1}H NMR spectrum of **3** confirms the presence of two [bta]$^-$ environments, with $\delta(^1H)$ = 7.93 and 7.21 ppm, and the trimethylsilyl protons occur at $\delta(^1H)$ = –0.08 ppm. The analogous resonances for **4** occur at $\delta(^1H)$ = 7.94 and 7.26 ppm, and the trimethylsilyl protons occur at $\delta(^1H)$ = 0.08 ppm. The ^{7}Li NMR spectra of **3** and **4** each feature a single resonance at $\delta(^7Li)$ = 2.43 ppm ($\omega_{1/2}$ = 28.7 Hz) and 2.00 ppm ($\omega_{1/2}$ = 50.9 Hz), respectively, suggesting that their polymetallic cage structures are not preserved in thf solution.

The reaction between [Li(hmds)], (bta)H and SnI_2 in toluene produced orange insoluble material. In thf solvent, however, a yellow solution and a precipitate formed. Filtration of the precipitate and concentration of the yellow solution led to the formation of yellow crystals, which X-ray diffraction revealed to be the ion-separated species [{(thf)$_2$Li(bta)}$_3${Li(thf)}]$_2$[SnI$_4$], [**5**]$_2$[SnI$_4$]. The molecular structure of the [{(thf)$_2$Li(bta)}$_3${Li(thf)}]$^+$ cation (**5**) (Fig. 2) can be regarded as a cyclic trimer analogue of the polymeric ladder complex [Li(bta)(thf)$_2$]$_\infty$,[5] in which the trimer 'crowns' a [Li(thf)]$^+$ cation. In the cyclic trimer component of **5**, Li(1), Li(3) and Li(4) reside in tetrahedral environments and are complexed by two benzotriazolate nitrogens and two thf ligands. The tetrahedral environment of Li(2) consists of three [bta]$^-$ nitrogens and one thf ligand. Thus, each [bta]$^-$ ligand in **5** adopts the [(bta)Li$_3$] coordination mode, with Li–N distances in the range 1.996(7)–2.049(7) Å (average 2.027 Å).

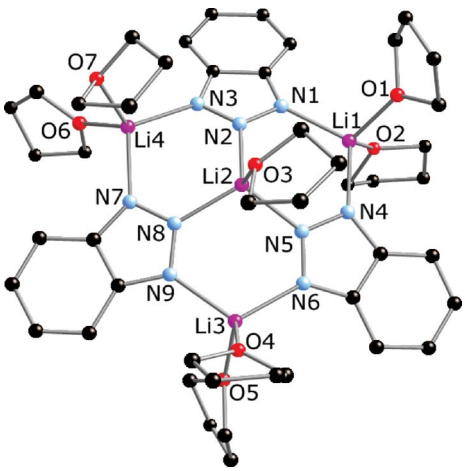

Fig. 2 Molecular structure of the cation [**5**]$^+$. Selected distances [Å]: Li(1)–O(1) 1.937(7), Li(1)–O(2) 1.947(7), Li(1)–N(1) 2.030(7), Li(1)–N(4) 2.032(7), Li(2)–O(3) 1.964(6), Li(2)–N(2) 2.021(6), Li(2)–N(5) 2.022(6), Li(2)–N(8) 1.996(7), Li(3)–O(4) 1.937(7), Li(3)–O(5) 1.939(7), Li(3)–N(6) 2.049(7), Li(3)–N(9) 2.042(6), Li(4)–O(6) 1.936(7), Li(1)–O(7) 1.996(7), Li(4)–N(3) 2.015(7), Li(4)–N(7) 2.033(7). Range of bond angles (average) [°]: Li(1)105.8(3)–114.7 (109.0), Li(2) 102.8(3)–113.9(3) (109.4), Li(3) 105.6(3)–114.8(3) (109.4), Li(4) 103.0(3)–112.5(3) (109.4).

The [SnI$_4$]$^{2-}$ anion in [**5**]$_2$[SnI$_4$] adopts a disphenoidal, or so-called "saw-horse", structure, which can be readily rationalized even with a simple VSEPR model that invokes a stereochemically active electron lone-pair on Sn(1) (Fig. 3). In the [SnI$_4$]$^{2-}$ anion, one of the iodine positions is disordered over two sites owing to the presence of a two-fold axis. Surprisingly, only two examples

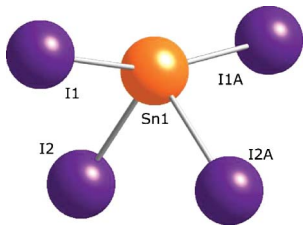

Fig. 3 Structure of the [SnI$_4$]$^{2-}$ anion in [**5**]$_2$[SnI$_4$]. Distances [Å] Sn(1)–I(1) 3.1874(3), Sn(1)–I(2). Angles [°] I(1)–Sn(1)–I(1A) 164.46(2), I(1)–Sn(1)–I(2) 95.812), I(2)–Sn(1)–I(2A) 98.72(2).

of the tetraiodostannate(II) dianion have been deposited in the Cambridge Structural Database.[10,11]

As with **3** and **4**, the low solubility of [**5**]$_2$[SnI$_4$] precluded a ^{119}Sn NMR spectrum, even in thf-d$_8$. The ^{1}H NMR spectrum of [**5**]$_2$[SnI$_4$] featured [bta]$^-$ environments with $\delta(^1H)$ = 7.91 and 7.17 ppm, and resonances due to coordinated thf at $\delta(^1H)$ = 3.58 and 1.73 ppm (overlapping with uncoordinated thf). The ^{7}Li NMR spectrum consists of a single broad resonance at $\delta(^7Li)$ = 2.46 ($\omega_{1/2}$ = 64.4 Hz). The presence of two lithium coordination environments in the solid-state structure of [**5**] but only a single ^{7}Li NMR resonance suggests that a dissociation-reassociation equilibrium of the [Li(bta)(thf)$_n$] units in **5** is taking place in thf.

Although use of the [hmds]$^-$ ligand in the chemistry of tin(II) is well developed,[12] complexes **3** and **4** are the first tin(II) complexes of the [bta]$^-$ ligand. Indeed, only one example of a Group 14 metal benzotriazolate complex has been crystallographically characterized, the polymeric lead(II) oxo complex [{Pb(bta)(μ-O)}$_2$]$_\infty$.[9] Crystallographically characterized alkali metal complexes of [bta]$^-$ are also scarce, being limited to the iron(II)-lithium complex **2**[7] and the coordination polymers [Li(bta)(dmso)]$_\infty$[5] and [K(bta)(hmpa)]$_\infty$.[6] The cation **5** differs from previously characterized alkali metal benzotriazolate complexes in the cyclic trimeric nature of its structure, whereas previously reported structures are based on lateral aggregation, or ring-laddering, structural motifs.[13]

The differing outcomes of reactions depicted in Scheme 1 are due in part to the differing properties of the Sn–X bonds within the series of tin(II) halides. The unreactive nature of SnF_2 is likely to be due to the Sn–F bonds in the solid-state polymer of tetramers [Sn$_4$F$_8$]$_\infty$,[14] which are evidently too strong to be transmetallated either by [Li(hmds)] or by [Li(bta)]. It is also possible that the poor solubility of SnF_2 contributes towards a barrier to reactivity.

The transmetallation chemistry of $SnCl_2$ and, to a lesser extent, $SnBr_2$, is probably the most common route into the metallo-organic chemistry of tin(II).[12] Indeed, several homoleptic tin(II) amido compounds of general formula [Sn(NR$_2$)$_2$] can be synthesized by this method.[15–17] The chloro and bromo ligands in $SnCl_2$ and $SnBr_2$ can therefore be readily substituted by [Li(hmds)] or by [Li(bta)], meaning that a simplified reaction mechanism can be proposed to account for the formation of **3** and **4** (Scheme 2).

A probable key step in the reactions that form **3** and **4** is deprotonation of (bta)H by [Li(hmds)] to generate [Li(bta)]. In another step, transmetallation of SnX_2 can form '[Sn(hmds)X]' (X = Cl, Br) as an intermediate species. Although the simplified mechanism does not account precisely for the relative amounts of tin, lithium, halide and benzotriazolate in **3** and **4**, a final, convergent step can be envisaged in which transmetallation of '[Sn(hmds)X]' by [Li(bta)] generates LiX as a by-product, and then the by-product

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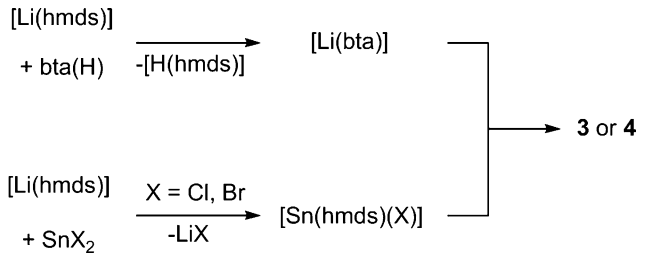

Scheme 2

is captured by the nascent tin(II) benzotriazolate units. The result of this process can also be regarded as the formation of a co-complex between a tin(II) amide and a lithium halide. Such systems could have potential applications as bimetallic reagents for E–H metallation reactions (E = C, N, O), in a manner analogous to that developed for lithium amide-halide co-complexes.[18]

The use of thf as the solvent in the synthesis of $[\mathbf{5}]_2[SnI_4]$ is likely to promote Schlenk-type equilibria. In solution, the Lewis acidity of SnI_2 can lead to the formation of $[SnI_4]^{2-}$, which crystallizes from thf with the cation **5** presumably as a result of their solubility being lower than that of other components of the Schlenk-type equilibria.

Conclusions

A one-pot synthetic method for the synthesis of tin(II) complexes of the benzotriazolate ligand has been developed. Whereas tin(II) fluoride was found to be unreactive with this method, the use of either tin(II) chloride or tin(II) bromide resulted in the formation of the cage complexes $[(hmds)_8Sn_8(bta)_{12}Li_8X_4]\cdot(n$ toluene) (X = Cl, n = x, **3**; X = Br, n = x, **4**). The requirement of the polar solvent thf for the analogous reaction between [Li(hmds)], (bta)H and SnI_2 promotes Schlenk-type equilibria, which results in the crystallization of $[\mathbf{5}]_2[SnI_4]$ as the least soluble component.

Our ongoing research will further develop the main group coordination chemistry of the benzotriazolate ligand.

Experimental

General considerations

All reactions were carried out using conventional Schlenk techniques. Reagents were obtained from commercial sources and used as supplied. Reaction solvents were either dried using an Innovative Technologies Solvent Purification System, or by refluxing over sodium-potassium alloy (toluene) or sodium benzophenone (thf). Solvents for NMR spectroscopy were distilled under nitrogen off sodium-potassium alloy or molten potassium, and were stored over 4 Å molecular sieves. Single crystal X-ray diffraction data were collected either on an Oxford Instruments XCalibur2 diffractometer or on an Oxford Instruments Super-Nova diffractometer. NMR spectra were acquired using a Bruker Avance III spectrometer operating at 400.13 MHz (^{1}H), 100.61 MHz (^{13}C) and 155.51 MHz (^{7}Li).

Synthesis of 3

A Schlenk tube was charged with [Li(hmds)] (0.67 g, 4.0 mmol), (bta)H (0.24 g, 2.0 mmol) and $SnCl_2$ (0.38 g, 2.0 mmol), and was cooled to −78 °C. Toluene (30 ml) was added and the reaction mixture stirred vigorously. Slowly warming the reaction to room-temperature over 30 min produced an orange solution and a precipitate. Filtration of the reaction (Celite, porosity 3) produced a darker orange solution. Careful evaporation of the solvent *in vacuo* resulted in the precipitation of a fine solid, which was redissolved on briefly heating the solution to reflux. Storage of the solution overnight at −30 °C produced yellow crystals of **3**·(8 toluene). Placing the crystals under vacuum for one hour results in the formation of polycrystalline 3 (0.16 g, 25%). Melting point: does not melt but develops a dark brown/black colour at *ca.* 170 °C. ^{1}H NMR (thf-d_8), 298 K, δ (ppm): 7.93, 2H, [bta]$^-$; 7.21, 2H, [bta]$^-$; −0.08, 48H, $SiMe_3$. ^{13}C NMR: 143.63, *ipso* [bta]$^-$; 124.06, [bta]$^-$ CH; 116.65, [bta]$^-$ CH; 1.89, $SiMe_3$. ^{7}Li NMR: 2.43 ppm. Elemental analysis calculated for $C_{120}H_{192}N_{44}Li_8Cl_4Si_{16}Sn_8$ (**3**): C 37.46, H 5.03, N 16.02; found C, 37.43 H 5.51, N 15.95%. Crystal data and structure refinement: $C_{176}H_{256}Cl_4Li_8N_{44}Si_{16}Sn_8$, 100(2) K, formula weight = 4584.65, triclinic, $P\bar{1}$, a = 18.3637(6) Å, b = 21.5801(6) Å, c = 30.8330(7) Å, α = 93.165(2)°, β = 98.775(2)°, γ = 112.991(3)°, V = 11027.7(5) Å^3, Z = 2, reflections collected 54522, independent reflections 37848 [R(int) = 0.0451], completeness to theta = 25.03° 97.1%, data/restraints/parameters 37848/0/2361, final R indices [$I > 2\sigma(I)$] R_1 = 0.0443 and wR_2 = 0.0856, R indices (all data) R_1 = 0.0851and wR_2 = 0.0944, largest diff. peak and hole 1.272 and −0.771 e.Å^{-3}.

Synthesis of 4

Complex **4** was synthesized in an identical manner to **3**, using [Li(hmds)] (0.67 g, 4.0 mmol), (bta)H (0.24 g, 2.0 mmol), $SnBr_2$ (0.56 g, 2.0 mol) and toluene (30 ml). The product, **4**·(3 toluene), was crystallized at −30 °C as yellow crystals. Placing the crystals under vacuum for one hour results in the formation of polycrystalline **4** (0.15 g, 22%). Melting point: does not melt but develops develops a dark brown/black colour at *ca.* 185 °C. ^{1}H NMR (thf-d_8), 298 K, δ (ppm): 7.94, 2H, [bta]$^-$; 7.26, 2H, [bta]$^-$; 0.08, 48H, $SiMe_3$. ^{13}C NMR δ (ppm): 144.16, *ipso* [bta]$^-$; 125.80, [bta]$^-$ CH; 116.22, [bta]$^-$ CH; 1.12, $SiMe_3$. ^{7}Li NMR, δ (ppm): 2.00. Elemental analysis calculated for $C_{120}H_{192}N_{44}Li_8Br_4Si_{16}Sn_8$ (**4**): C 35.81, H 4.81, N 15.31; found C 35.69, H 5.29, N 15.19%. Crystal data and structure refinement $C_{141}H_{218}Br_4Li_8N_{44}Si_{16}Sn_8$, 123(1) K, formula weight = 4303.84, triclinic, $P\bar{1}$, a = 19.1397(3) Å, b = 20.9948(3), c = 26.6822(5) Å, α = 92.659(1)°, β = 95.907(1)°, γ = 111.672(2)°, V = 9869.6(3) Å^3, Z = 2, reflections collected 82702, independent reflections 39316 [R(int) = 0.0769], completeness to theta = 76.01° = 95.3%, data/restraints/parameters 39316/24/2071, final R indices [$I > 2\sigma(I)$] R_1 = 0.0614 and wR_2 = 0.1542, R indices (all data) R_1 = 0.1027 and wR_2 = 0.1695, largest diff hole and peak −3.040, 3.031 eÅ^{-3}.

Synthesis of $[\mathbf{5}]_2[SnI_4]$

The same synthetic procedure used for the synthesis of **3** and **4** was used to prepare $[\mathbf{5}]_2[SnI_4]$, but with thf (20 ml) as the solvent. Combining [Li(hmds)] (0.33 g, 2.0 mmol), (bta)H (0.12 g, 1.0 mmol), SnI_2 (0.37 g, 1.0 mmol) and working-up the reaction as described above allowed yellow crystals of $[\mathbf{5}]_2[SnI_4]\cdot$(thf) to be obtained at room-temperature. Placing the yellow crystals under vacuum resulted in the formation of polycrystalline $[\mathbf{5}]_2[SnI_4]$

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(0.56 g, 23%). Melting point: does not melt but develops develops a brown colour at *ca.* 200 °C. ^{1}H NMR (thf-d_8), 298 K, δ (ppm): 7.91, 2H, [bta]$^-$; 7.17, 2H, [bta]$^-$; 3.58, accurate integration not possible owing to overlap with solvent resonance, coordinated thf; 1.73, coordinated thf. ^{13}C NMR: 123.20, [bta]$^-$ CH; 116.79, [bta]$^-$ CH; 68.1, coordinated thf; 26.3 coordinated thf. ^{7}Li NMR: 2.45 ppm. Elemental analysis calculated for $C_{92}H_{136}N_{18}Li_8O_{14}I_4Sn$: C 46.04, H 5.71, N 10.50; found C 46.19, H 5.79, N 10.63%. Crystal data and structure refinement: $C_{96}H_{144}I_4Li_8N_{18}O_{15}Sn$, 123(1) K, formula weight = 2472.12, orthorhombic, *Fdd*2, a = 37.5021(5) Å, b = 47.4100(7) Å, c = 12.6919(2) Å, V = 22565.9(6) Å^3, Z = 8, reflections collected 27163, independent reflections 9029 [R(int) = 0.0334], completeness to theta = 74.26° 98.7%, data/restraints/parameters 9029/1/676, final R indices [$I > 2\sigma(I)$] R_1 = 0.0352 and wR_2 = 0.0942, R indices (all data) R_1 = 0.0359 and wR_2 = 0.0947, absolute structure parameter 0.006(4), largest diff. peak and hole 0.954 and −1.187 e.Å^{-3}.

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